energies

Supplementary Materials

Ethanol-Assisted Hydrothermal Liquefaction of Poplar Using $Fe-Co/Al_2O_3$ as Catalyst

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Abstract: Although the conversion of lignocellulosic biomass into bio-oil with high yield/quality through hydrothermal liquefaction (HTL) is promising, it still faces many challenges. In this study, a $Fe_x-Co_{(1-x)}/Al_2O_3$ catalyst was prepared with the coprecipitation method and low-content ethanol was used as the cosolvent for the HTL of poplar. The results showed that the $Fe_x-Co_{(1-x)}/Al_2O_3$ catalyst significantly promoted the yield and energy recovery rate (ERR) of bio-oil compared with the control (10% ethanol content). At 260 °C for 30 min, $60Fe-40Co/Al_2O_3$ had the best catalytic effect, achieving the highest bio-oil yield (67.35%) and ERR (93.07%). As a multifunctional bimetallic catalyst, $Fe_x-Co_{(1-x)}/Al_2O_3$ could not only increase the degree of hydrogenation deoxidization of the product but also promote the diversity of phenolic compounds gained from lignin. The bio-oil obtained from HTL with $Fe_x-Co_{(1-x)}/Al_2O_3$ as catalyst contained lower heterocyclic nitrogen, promoting the transfer of more bio-oil components to substances with lower boiling point.

Keywords: hydrothermal liquefaction; bimetallic cocatalysis; bio-oil; low ethanol ratio; poplar

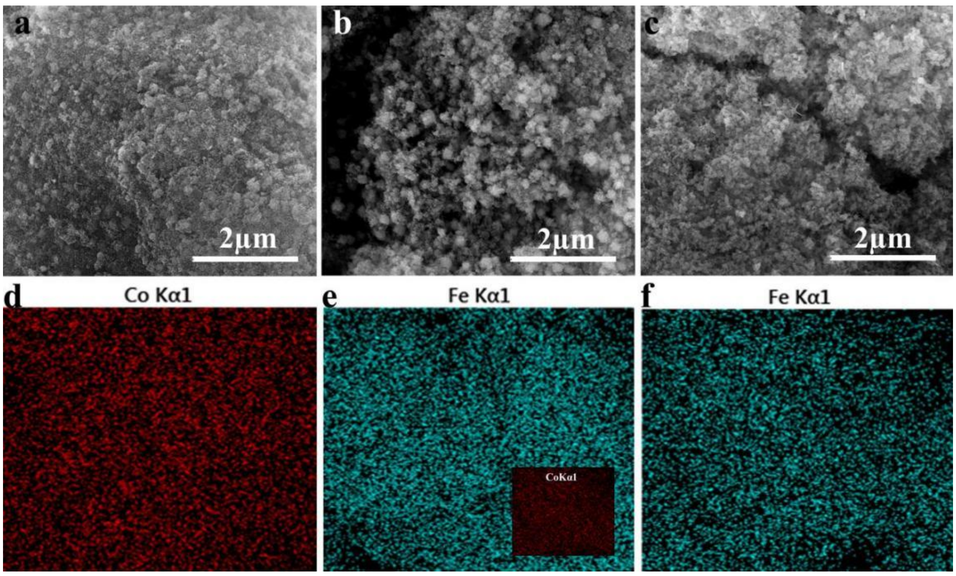


Figure S1. SEM and EDS (Fe, Co element) images of $100Fe/Al_2O_3$ (**a, d**), $60Fe-40Co/Al_2O_3$ (**b, e**), and $100Co/Al_2O_3$ (**c, f**).

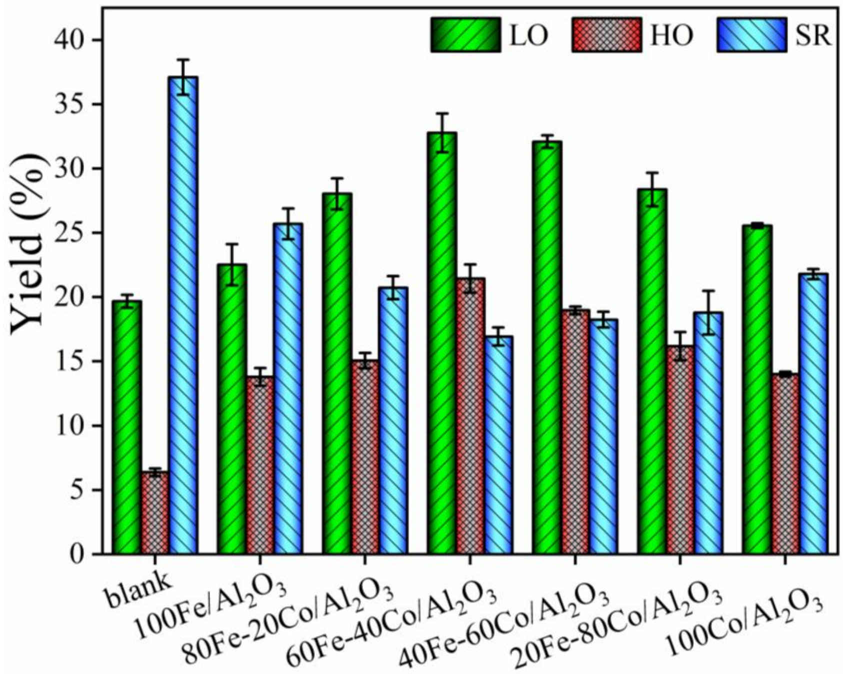


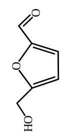
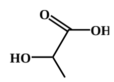
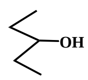
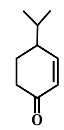
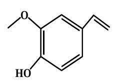
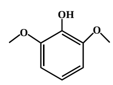
Figure S2. Product distribution of catalytic HTL without ethanol (260 °C, 30 min).

Table S1. GC-MS analysis of bio-oil catalyzed by 60Fe-40Co/Al2O3 (260 °C, 30 min）.

No.	Compound name	Formula	Relative peak area (%)	
			HO	LO
1	Acetic acid, butyl ester	$C_6H_{12}O_2$	1.61	—
2	Furfural	$C_5H_4O_2$	1.47	—
3	2-Pentanone, 4-hydroxy-4-methyl-	$C_6H_{12}O_2$	0.99	—
4	2-Cyclopenten-1-one, 2-methyl-	C_6H_8O	1.16	—
5	2-Furancarboxaldehyde, 5-methyl-	$C_6H_6O_2$	0.52	—
6	Phenol	C_6H_6O	17.34	1.44
7	2H-Tetrazol-2-ethanal, 5-methyl-	$C_4H_6N_4O$	0.53	—
8	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	$C_6H_8O_2$	2.42	—
9	Acetohydrazide, 2-hydroxy-2-phenyl-N2-but-2-enylideno-	$C_{12}H_{14}N_2O_2$	0.52	—
10	Phenol, 2-methyl-	C_7H_8O	1.01	—
11	Phenol, 2-methoxy-	$C_7H_8O_2$	2.49	—
12	Benzofuran, 2-methyl-	C_9H_8O	0.76	—
13	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-	$C_7H_{10}O_2$	0.58	1.25
14	1-Octanol	$C_8H_{18}O$	0.65	1.04
15	Phenol, 2-methoxy-4-methyl-	$C_8H_{10}O_2$	0.66	—
16	Dodecane	$C_{12}H_{26}$	1.48	—
17	1,2-Benzenediol	$C_6H_6O_2$	0.59	5.17
18	2-Furancarboxaldehyde, 5-(hydroxymethyl)-	$C_6H_6O_3$	1.18	3.54
19	Phenol, 4-ethyl-2-methoxy-	$C_9H_{12}O_2$	2.12	—
20	Bicyclo[3.3.1]nona-3,7-diene-2,9-dione	$C_9H_8O_2$	0.73	—
21	Phenol, 2,6-dimethoxy-	$C_8H_{10}O_3$	6.43	3.40
22	Phenol, 2-methoxy-3-(2-propenyl)-	$C_{10}H_{12}O_2$	1.82	—
23	Benzaldehyde, 2-hydroxy-4-methyl-	$C_8H_8O_2$	0.60	—
24	Tetradecane	$C_{14}H_{30}$	1.99	—
25	Benzaldehyde, 3-hydroxy-4-methoxy-	$C_8H_8O_3$	1.74	—
26	Phenol, 2-methoxy-4-(2-propenyl)-, acetate	$C_{12}H_{14}O_3$	2.99	—
27	Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-	$C_9H_{10}O_3$	0.59	—
28	Benzene, 1,1'-(1,2-ethanediyl) bis-	$C_{14}H_{14}$	1.45	—
29	Benzene, 1,2,3-trimethoxy-5-methyl-	$C_{10}H_{14}O_3$	1.31	—

30	2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-	$C_{10}H_{12}O_3$	1.65	—
31	Heptadecane	$C_{17}H_{36}$	1.96	—
32	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	$C_{11}H_{14}O_3$	4.51	—
33	2,4-Hexadienedioic acid, 3,4-diethyl-, dimethyl ester, (E, Z)-	$C_{12}H_{18}O_4$	0.99	—
34	Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	$C_9H_{10}O_4$	2.27	—
35	Benzoic acid, 2,4-bis[(trimethylsilyl)oxy]-, trimethylsilyl ester	$C_{16}H_{30}O_4Si3$	1.88	—
36	3-Buten-2-one, 4-(2,2-dimethyl-6-methylenecyclohexyl)-	$C_{13}H_{20}O$	0.81	—
37	Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	$C_{10}H_{12}O_4$	1.98	—
38	(S)-2-Hydroxypropanoic acid	$C_3H_6O_3$	—	14.28
39	2,5-Hexanedione	$C_6H_{10}O_2$	—	0.54
40	Propane, 2-ethoxy-	$C_5H_{12}O$	—	1.52
41	3-Pentanol	$C_5H_{12}O$	—	4.22
42	2-Hydroxy-gamma-butyrolactone	$C_4H_6O_3$	—	1.96
43	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	$C_6H_8O_2$	—	5.12
44	3-Buten-2-ol	C_4H_8O	—	0.57
45	2-Oxo-n-valeric acid	$C_5H_8O_3$	—	8.31
46	Pentanoic acid, 4-oxo-	$C_5H_8O_3$	—	1.19
47	Butanal, 3-methyl-	$C_5H_{10}O$	—	2.11
48	Propiolactone	$C_3H_4O_2$	—	0.87
49	2-Cyclohexen-1-one, 4-(1-methylethyl)-	$C_9H_{14}O$	—	2.18
50	1,2-Benzenediol, 4-methyl-	$C_7H_8O_2$	—	2.56
51	2-Isopropylidene-5-methylhex-4-enal	$C_{10}H_{16}O$	—	0.66
52	Cyclohexanethiol, 2-ethyl-, acetate	$C_{10}H_{18}OS$	—	0.77
53	1,4-Benzenediol, 2-methyl-	$C_7H_8O_2$	—	0.96
54	p-Nitrophenyl hexanoate	$C_{12}H_{15}NO_4$	—	1.26
55	Vanillin	$C_8H_8O_3$	—	1.30
56	1,4-Benzenediol, 2,6-dimethyl-	$C_8H_{10}O_2$	—	1.33
57	Ethanone, 1-(1-cyclohexen-1-yl)-	$C_8H_{12}O$	—	1.25
58	Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-	$C_9H_{10}O_3$	—	1.60
59	1H-Indene-1,5(6H)-dione, 2,3,7,7a-tetrahydro-7a-methyl-	$C_{10}H_{12}O_2$	—	1.90
60	2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-	$C_{10}H_{12}O_3$	—	1.45
61	3,4,5-Trimethyl-1H-pyrano[2,3-c] pyrazol-6-one	$C_9H_{10}N_2O_2$	—	1.54
62	Bicyclo [2.2.2] octa-2,5-diene, 1,2,3,6-tetramethyl-	$C_{12}H_{18}$	—	1.52
63	Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	$C_9H_{10}O_4$	—	1.23
64	Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	$C_{10}H_{12}O_4$	—	0.87
65	2,4-Hexadienedioic acid, 3,4-diethyl-, dimethyl ester, (E, Z)-	$C_{12}H_{18}O_4$	—	0.74

Table S2. Changes in the content of part of the compounds in LO and HO under different catalytic conditions (260 °C, 30 min).

Catalyst	**LO (%)**					
						
Blank	**8.36**	**0**	**0**	**0**	**5.48**	**16.39**
100Fe/Al_2O_3	0	12.75	3.97	0	0	11
80Fe-20Co/Al_2O_3	1.93	3.36	6.44	2.21	0	9.4
60Fe-40Co/Al_2O_3	3.54	14.28	4.22	2.18	0	9.83
40Fe-60Co/Al_2O_3	2.19	16.09	5.15	1.53	0	11.42
20Fe-80Co/Al_2O_3	0.53	11.11	4.91	2.1	0	12.82
100Co/Al_2O_3	0	16.26	6.22	2.02	0	14.07
Catalyst	HO (%)					

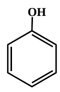
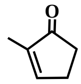
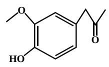
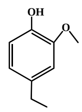
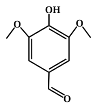
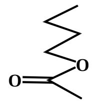
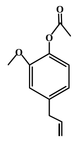
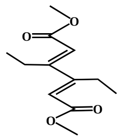
								
Blank	16.55	0	0	0	4.53	0	0	0
100Fe/Al_2O_3	10.36	2.56	0	1.18	0	0	0	1.17
80Fe-20Co/Al_2O_3	18.57	2.33	1.31	1.41	2.87	2.13	0.15	1.43
60Fe-40Co/Al_2O_3	17.34	1.65	1.65	2.12	2.27	1.61	2.19	0.99
40Fe-60Co/Al_2O_3	14.43	1.46	2.05	1.34	3.5	1.74	2.57	1
20Fe-80Co/Al_2O_3	15.51	0	1.71	0	2.6	1.57	3.2	1.17
100Co/Al_2O_3	19.2	0	1.44	0	0	1.53	3.36	2.2

Table S3. Functional group distribution of bio-oil.

Number	Wavenumber/cm^{-1}	Band Assignment	Functional groups
1, 8	3700-3150	O-H/N-H/C-H	Phenols, fatty, alcohol, N-containing heterocyclic compounds
2, 9	3000-2800	C-H	Methyl and methylene groups
3, 10	1800-1680	C=O	Ester carbonyl，carboxylic acids，aldehydes，ketons
4, 11	1680-1540	C=C	Aromatic
12, 13	1540-1480	C=C	Aromatic
5	1480-1350	C-H	Esters
14	1375-1150	C-O/O-H	Esters，ketone，carboxylic acid
7, 15	1160-1030	C-O	Fatty ether
16	1040-980	C-O	Esters，ketone

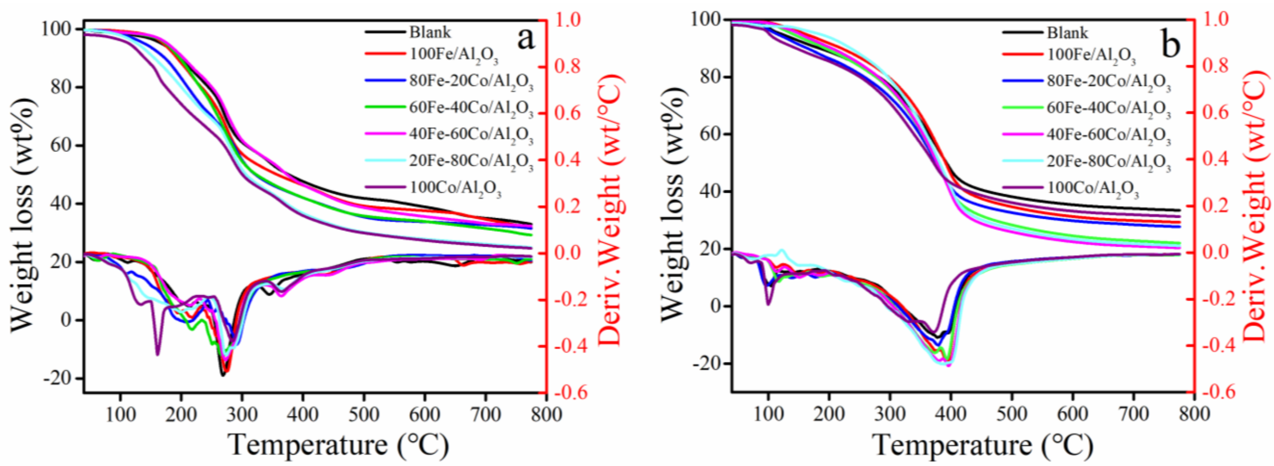


Figure S3. TGA–DTG curves of bio-oil under different liquefaction conditions at 260 °C and 30 min (**a**) LO; (**b**) HO.